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Abstract

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DUPLICADO

#### Forming a Coating on a Substrate

Field of the invention

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The present invention relates to a process for forming a coating, preferably, an oxide layer on a substrate. In particular, though not exclusively, the present invention relates to a process for anodising an aluminium substrate.

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#### Background

Metals such as aluminium are often anodised to provide them with an oxide coating. In a conventional anodising process, an aluminium substrate is employed as the anode of an electrochemical cell. This anode is connected to a cathode, via an electrolyte of, for example, sulphuric acid. When a current is passed through the cell, a coating of aluminium oxide is formed on the anode.

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Conventional anodising processes operate at current densities of 1 to 2 amps per dm<sup>2</sup>. At such low current densities, the impedance at the anode/electrolyte interface is significantly higher than that of the electrolyte. In fact, as the thickness of the anodised oxide layer increases, the impedance at the anode/electrolyte interface increases. Thus, any area of the anode that is more thinly coated will present less impedance to current flow.

Consequently, the current density at that region is higher, causing the rate of oxide formation at that particular point to rise until the thickness of the anodised coating matches that of the remainder of the work piece. Thus, conventional

anodising processes are self-leveling, and result in anodised coatings that are substantially uniform in thickness.

5 Anodised oxide coatings that are uniform in thickness are useful in many applications. However, it has now been found that it may sometimes be advantageous to produce anodised coatings of varying thickness. The latter is particularly true when anodising loudspeaker diaphragms, including loudspeaker cones.

Loudspeaker diaphragms have characteristic resonances, which are determined by the dimension, stiffness and density of the diaphragm. These characteristic resonances have the effect of making the sounds emitted by the loudspeaker sound harsh, at the frequencies at which these resonances occur.

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Aluminium has been used for the manufacture of loudspeaker diaphragms, and in particular, loudspeaker cones for a number of years. An aluminium cone itself, however, tends to have a characteristic resonance within the audible frequency range. Thus, the sounds emitted by the loudspeaker diaphragm at the characteristic resonant frequencies are harsh. This has a negative effect on the acoustic performance of the cone.

To ameliorate this problem, the aluminium cone may be anodised. The oxide layer formed on the surface of the cone increases the stiffness of the overall structure, causing the loudspeaker diaphragm's characteristic resonances to increase within the audible frequency range, thus extending

the usable bandwidth of the loudspeaker. Consequently, the acoustic performance of the cone is improved.

Anodising, however, can have a negative effect on the

5 strength of the cone. This is because metal is consumed from
the surface during the anodising process, resulting in a
thinner, and consequently, weaker structure. This weakness
is particularly apparent in the cylindrical or "neck" region
of the cone, where the voice coil former is typically

10 attached. Accordingly, it is particularly desirable to
ensure that the thickness of the oxide coating in this
particular region is reduced.

This may be achieved by carrying out the anodising process
in two separate steps. For example, the loudspeaker
diaphragm may be anodised to form a coating of a
predetermined thickness. Thereafter, the cylindrical region
may be masked, leaving the conical region of the cone
exposed. The masked cone may then be anodised further. In
this way, the thickness of the coating in the conical region
of the cone is greater than that in the cylindrical region
of the cone.

Summary of the invention

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A new process for forming an oxide layer that is non-uniform in thickness has now been developed.

According to the present invention, there is a process for forming a coating on a substrate, said process comprising:

providing an electrochemical cell comprising a cathode and an electrolyte,

connecting a substrate to be anodised as the anode of the cell,

passing a current through the cell, such that a coating is formed on the substrate,

- controlling the current density distribution within the cell, such that the coating is formed more rapidly in one region of the substrate than in another region of the substrate.
- 10 Preferably, the coating is formed of a boride, nitride or oxide. More preferably, the coating is formed of an oxide.

Preferably, the coating is formed by anodising.

Alternatively, the Keronite process may be employed.

Brief description of the figures

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These and other aspects of the invention will now be described with reference to the accompanying drawings, in which:

Figure 1 is a schematic, cross-sectional view of an apparatus that is suitable for anodising a loudspeaker diaphragm in accordance with a first embodiment of the present invention,

Figure 2 is a schematic diagram of a section of an anodised loudspeaker diaphragm,

30 Figure 3 is a schematic, cross-sectional view of an apparatus that is suitable for anodising a disc in

accordance with a second embodiment of the present invention.

Detailed description of the invention

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The present invention relates to a process for forming an oxide layer on a substrate.

The process of the present invention may be an anodising 10 process.

The process of the present invention may be employed to produce an oxide layer that is thicker in one region of the substrate than in another region of the substrate.

15 Preferably, the oxide layer tapers from a maximum value in one region of the substrate to a minimum value in another region of the substrate.

Without wishing to be bound by any theory, it is believed

that the current density distribution within the cell may be controlled at least in part by operating the cell at current densities above those employed in conventional anodising processes. At current densities above those conventionally employed, the voltage drop within the electrolyte is increased with respect to that at the electrolyte/anode interface. Thus, the current density at the surface of the anode varies, depending on the current path length between the cathode and anode. Current path length may be regarded as the distance that charge has to travel to reach a

particular region of the anode from the cathode. In general, therefore, the greater the distance between the cathode and the anode, the greater the current path length.

The current density along the substrate is greatest where the current path length is at a minimum, and smallest where the current path length is at a maximum. Thus, when the cell is operated at current densities higher than those conventionally employed, it is possible to control the current density across the anode substrate by ensuring that the current path length between the cathode and the anode substrate varies from one region of the anode to another.

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Oxide layers form most rapidly in regions where the local current density is high, and least rapidly where the local current density is low. Thus, in a given time frame, the thickness of the oxide layer will vary across the substrate.

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In the process of the present invention, a current is passed through the cell by connecting the substrate and the cathode to a power source. The current density employed is preferably above 5 amps per dm<sup>2</sup>, for example, from 10 to 200 amps per dm<sup>2</sup>, preferably, 60 to 150 amps per dm<sup>2</sup>, more preferably, 80 to 100 amps per dm<sup>2</sup>. The current density may be maintained at 90 amps per dm<sup>2</sup>.

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The substrate may be formed of any anodisable material. Suitable materials include aluminium, titanium, magnesium and alloys of at least one of aluminium, magnesium and titanium. Preferably, an aluminium substrate is employed. The substrate may be any suitable substrate that requires anodising, for example, a loudspeaker diaphragm.

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The cathode may be formed of a suitable metal, for example, titanium, aluminium, and stainless steel. Such metals are

particularly suitable when sulphuric acid is used as electrolyte.

Any suitable electrolyte may be employed in the process of the present invention. For example, the electrolyte may be sulphuric acid, chromic acid, oxalic acid, sulphosalysilic acid, and phosphoric acid. Of these electrolytes, sulphuric acid is preferred. For example, when sulphuric acid is employed as the electrolyte, the electrolyte concentration may be 100 to 400 g/l of sulphuric acid and 5 to 30g/l aluminium, for example, 200 to 300g/l of sulphuric acid and 10 to 20g/l aluminium.

Where sulphuric acid is employed as an electrolyte, the

temperature of the electrolyte may be at 0 to 100 degrees C.

Preferably, the electrolyte is heated above room

temperature, for example, at 30 to 80 degrees C, more

preferably, 50 to 60 degrees C. In a preferred embodiment,

the electrolyte temperature is 45 to 55 degrees C. Without

wishing to be bound by any theory, it is believed that

increasing the electrolyte temperature causes an increase in

the impedance of the electrolyte relative to the impedance

at the electrolyte/anode interface.

The electrolyte may be passed over the surface of the substrate. Advantageously, passing the electrolyte over the substrate in this manner removes heat generated by the process away from the surface of the substrate. In a preferred embodiment, the electrolyte is pumped through the electrochemical cell, for example, via an inlet and outlet in the electrolyte tank. The electrolyte may be passed over the surface of the substrate at any suitable rate. For

example, the surface velocity of the electrolyte over the substrate may be 10 to 1000 metres per minute. The specific surface velocity of the electrolyte over the substrate is preferably 100 to 200 metres per minute, for example, 120 metres per minute.

The electrochemical cell may be provided with a mask to control the current path length between the cathode and the anode. For example, a mask may be between the cathode and the anode to increase the current path length between cathode and the anode. In this way, the current density of the region of the anode shielded by the mask is reduced. This results in a corresponding decrease in the rate of oxide formation in this region. By varying the size, geometry and/or position of the mask relative to the substrate, the variation in thickness of the oxide layer may be controlled.

The mask may be formed of any suitable material, for

20 example, a plastic material, such as polypropylene. At least
part of the mask may also be formed of a metal or other
electrically conducting material. The electrically
conducting portion of the mask may be coupled to the
cathode.

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The distance between the mask and the substrate may be 0.1 to 400 mm, more preferably, 0.1 to 50 mm. It should be noted, however, that the distance between the mask and the substrate is dependent on a number of factors, such as the size of the substrate.

According to a preferred embodiment of the present invention, there is provided a process for forming a coating, preferably, an oxide layer on a loudspeaker diaphragm, said method comprising:

5 providing an electrochemical cell comprising a cathode and an electrolyte,

connecting a loudspeaker diaphragm as the anode of the cell,

passing a current through the cell, such that an oxide 10 layer is formed on the loudspeaker diaphragm, and

controlling the current density distribution within the cell, such that the oxide layer is formed more rapidly in one region of the diaphragm than in another region of the diaphragm.

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Preferably, the coating is formed on the loudspeaker diaphragm by anodising. Alternatively, the Keronite process may be employed.

The process above may be used to produce an oxide layer that is thicker in one region of the loudspeaker diaphragm than another. For example, where the loudspeaker diaphragm is a loudspeaker cone of conventional shape, the oxide layer tapers from a maximum thickness in one region of the cone to a minimum value in another region of the cone.

The current density distribution within the cell may be controlled by operating the cell at current densities above those conventionally employed. For example, the cell may be operated at current densities of above 5 amps per dm<sup>2</sup>, for example, from 10 to 200 amps per dm<sup>2</sup>, preferably, 60 to 150

amps per dm<sup>2</sup>, more preferably, 80 to 100 amps per dm<sup>2</sup>. The current density is preferably maintained at 90 amps per dm<sup>2</sup>.

At current densities above those conventionally employed, the voltage drop within the electrolyte is increased with respect to that at the electrolyte/anode interface. Thus, the current density along the diaphragm varies, depending on the current path length between the cathode and the diaphragm. Since current path length varies depending on the 10 distance between the cathode and the anode, regions of the diaphragm that are close to the cathode tend to have high local current densities. Conversely, regions of the diaphragm that are further away from the cathode tend to have lower local current densities. Since oxide growth occurs more rapidly where the local current density is high, oxide growth is likely to occur more rapidly in certain regions of the diaphragm than in others. In a given time frame, therefore, the oxide layer is likely to be thickest in certain regions of the diaphragm than in others.

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A mask may be positioned between the cathode and the loudspeaker diaphragm to control the current path length between the cathode and the diaphragm. Thus, a mask may be employed to control the variation in thickness of the oxide layer formed on the diaphragm. By varying the size, geometry and/or position of the mask relative to the substrate, the variation in thickness of the oxide layer may be controlled.

Preferably, a flow of electrolyte is passed over the surface 30 of the loudspeaker diaphragm. As mentioned above, passing the electrolyte over the substrate in this manner, removes the heat generated by the oxidation process away from the

surface of the substrate. In one embodiment, the electrolyte is pumped through a channel defined by the substrate and the mask. By controlling the direction of flow of electrolyte between the cathode and the anode, the current path length between the cathode and the anode may also be varied.

The loudspeaker diaphragm may be formed of any suitable material, preferably, an anodisable material, such as aluminium, titanium, magnesium and/or alloys of one or more of aluminium, titanium, magnesium. Preferably, aluminium is employed. The diaphragm may be formed using any suitable method for producing loudspeaker diaphragms. For example, pressing and/or spinning techniques may be employed.

15 The loudspeaker diaphragm employed in the method above preferably has a conventional shape. Thus, the loudspeaker diaphragm may be a conventional loudspeaker cone comprising a generally cylindrical region (the "neck" region) and a generally conical region.

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The oxide layer in the conical region of the diaphragm is preferably thicker than the oxide layer in the cylindrical region of the diaphragm. Preferably, the oxide layer tapers from a minimum value in the cylindrical region of the diaphragm to a maximum value in the conical region of the diaphragm. The oxide layer in the cylindrical region may itself be tapered. Alternatively, the oxide layer in the cylindrical region is substantially uniform in thickness. For example, only the oxide layer in the conical region or 30 part of the conical region of the diaphragm is tapered.

The thickness of the oxide layer in the cylindrical region may be 0.1 to 8 microns, preferably, 1 to 4 microns, for example, about 2 to 3 microns. The thickness of the oxide layer in the conical region may be 2 to 50 microns,

5 preferably, 8 to 40 microns, for example, about 10 to 20 microns. The minimum thickness of the oxide layer may be 4 to 40 % of the maximum thickness of the oxide layer. In a preferred embodiment, the coating is 1 to 3 microns thick in the cylindrical region of the diaphragm, and 9 to 12 microns thick at the periphery of the conical region of the diaphragm. It should be noted that the angle of taper is dependent upon the size and profile of the diaphragm. Thus, the angle of taper will be different for different size diaphragms.

The thickness of the coating may be determined by any suitable method; that selected will be influenced by the purpose of the particular measurement. Preferably, the thickness is measured over an average area of 0.01 to 1 cm<sup>2</sup>, more preferably, 0.1 to 0.8 cm<sup>2</sup>, most preferably, 0.2 to 0.5 cm<sup>2</sup>, for example, 0.25 cm<sup>2</sup>.

For example, to determine the average thickness of the coating over the entire surface of the diaphragm, the diaphragm is weighed and then stripped of the coating. Any suitable method may be employed to strip the diaphragm: for example, an acid, such as phosphoric and/or chromic acid may be employed to strip the diaphragm, in accordance with British DEF STAN 03-25. The stripped diaphragm is then weighed. The difference between the weight of the coated diaphragm and the stripped diaphragm is then that of the coating. The total surface area of the diaphragm is then

calculated. Provided the density of the coating (e.g. aluminium oxide) is known, it is possible to calculate the average thickness of the coating.

5 Alternatively, the thickness at any particular part of the diaphragm may be established by measuring the overall thickness of the coated diaphragm using a micrometer. The diaphragm may then be stripped using any suitable method (e.g. British DEF STAN 03-25). The thickness of the stripped diaphragm is then measured. The difference between the two 10 thickness measurements is the total thickness of the coating. Thus, if the diaphragm is coated on both its inner and outer surface, the difference corresponds to the total thickness of the inner and outer coating. If it can be assumed that both coatings are equal in thickness, the 15 difference between the thickness of the coated and uncoated diaphragms can be halved to give the thickness of each coating. However, if it is necessary to establish the coating thickness on the one surface of the diaphragm without reference to the other, the surface not to be 20 measured may be protected from the stripping solution by a suitable masking technique, such a stopping-off lacquer or protective tape, so that the difference in micrometer readings is that of the required coating.

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Other methods of measuring coating thickness include (not exclusively) use of eddy-current devices, calibrated microscope focussing successively on the anodised surface and that of the underlying metal. It should be noted that some methods might not be applicable in certain circumstances.

The oxide layer may be formed on both the inner and outer surfaces of the diaphragm. For the avoidance of doubt, the inner surface of the diaphragm is the surface of the diaphragm to which the dome and/or voice coil former is typically attached and which typically faces the listener. The outer surface of the diaphragm is the opposite surface of the diaphragm to which, for example, a spider is typically connected.

An oxide layer may be formed on the inner and outer surfaces the diaphragm in two separate anodising steps.

Alternatively, the inner and outer surfaces of the diaphragm may be coated in a single anodising process. This may be achieved by connecting separate power supplies to the inner and outer surfaces of the diaphragm. For example, one power supply may be coupled to the inner surface of the diaphragm and a cathode, and a separate power supply may be coupled to the outer surface of the diaphragm and a different cathode. By operating the two "cells" at different current densities, the oxide layers on the inner and outer surfaces of the diaphragm may be varied independently. Alternatively, both "cells" may be operated under the same conditions.

Preferably, the same electrolyte may be used in both 25 "cells".

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The oxide layer on both surfaces of the may be thinner in the cylindrical region of the diaphragm. Alternatively, the oxide layer on only one of the surfaces of the diaphragm may be thinner at the cylindrical region of the diaphragm. This oxide layer is preferably located on the inner surface of the diaphragm (i.e. the surface of the diaphragm to which a loudspeaker dome is typically attached).

In an alternative embodiment of the invention, the oxide layer is only formed on one surface of the diaphragm.

Preferably, the oxide layer is formed on the inner surface of the diaphragm.

The loudspeaker diaphragm may be of a uniform thickness

prior to the formation of the oxide layer. The oxidation

method, however, may cause the diaphragm substrate to become

non-uniform in thickness. For example, when a metal (e.g.

aluminium) diaphragm is anodised, some of the metal at the

surface of the diaphragm is consumed to form the oxide

15 layer. As a result, the metal diaphragm becomes thinner in

the regions where the anodically formed oxide layer is

applied. Typically, the thicker the anodically formed oxide

layer, the more surface metal is consumed. When the oxide

layer is tapered in cross section, the diaphragm substrate

is correspondingly inversely tapered.

In an alternative embodiment, the diaphragm may be non-uniform in thickness prior to coating. For example, some parts of the diaphragm (e.g. the neck region) may be marginally thinner than other parts due to the process employed to produce the diaphragm.

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The diaphragm anodised in accordance with the method herein described may be incorporated into any suitable loudspeaker.

Suitable loudspeakers include: sub woofers, bass, and midrange loudspeakers. The diaphragm described above may

also be suitable for use in loudspeakers for automobile applications.

Referring to Figure 1, there is provided an apparatus 10 for carrying a process in accordance with a first embodiment of the present invention. The apparatus 10 comprises a casing 12, cathodes 14a, 14b an inlet 16 and an outlet 18. The substrate, a loudspeaker diaphragm 20, is employed as the anode of the apparatus 10. The apparatus 10 is provided with an electrolyte 22 of sulphuric acid. Masks 24a, 24b are positioned in spaced relation to the diaphragm 20. Mask 24a may be conical in shape. The diaphragm 20 and the cathode 14 are both formed of aluminium.

15 The apparatus 10 may include additional components, which are not shown in the drawing for reasons of clarity.

In operation, the electrolyte 22 is pumped through the apparatus 10 via the inlet 16 and outlet 18. The electrolyte flows through channels defined by the masks 24a, 24b and the diaphragm 20, as shown by the arrows "a". In this way, a flow of electrolyte 22 is passed over both the inner and outer surfaces of the diaphragm 20.

A power supply (not shown) is connected to the cathode 14a and the inner surface of the diaphragm 20. A separate power supply (not shown) is connected to the cathode 14b and the outer surface of the diaphragm 20. In this way, the inner surface of the diaphragm 20 and the cathode 14a form the electrodes of a first electrochemical cell, whilst the outer surface of the diaphragm 20 and the cathode 14b form the electrodes of a second electrochemical cell.

The first electrochemical cell may be operated at a current density of 90 Amps per dm<sup>2</sup>. At this current density, the voltage drop within the electrolyte is high compared to that at the electrolyte/anode interface. Thus, the current density along the diaphragm 20 varies, depending on the current path length between the cathode 14a and the inner surface of the diaphragm 20.

- Because of the relative geometry and location of the mask 10 24a, the distance between the cathode 14a and the inner surface of the diaphragm 20 tapers from a minimum at the periphery 20b of the diaphragm 20, to a maximum at the neck region 20a of the diaphragm 20. The current path length, 15 therefore, tapers in a corresponding manner. Accordingly, the local current density at the inner surface of the diaphragm 20 tapers in reverse i.e. from a maximum at the periphery 20b of the diaphragm 20 to a minimum at the neck region 20a of the diaphragm 20. Since the rate of oxide 20 formation is highest where the local current density is at a maximum, the rate of oxide layer formation tapers from a maximum at the periphery 20b of the diaphragm 20 to a minimum at the neck region 20a of the diaphragm 20.
- 25 The second electrochemical cell may be operated at the same current density as the first electrochemical cell. Because of the relative position and geometry of the mask 24b, however, the effective distance between the outer surface of the diaphragm 20 and the cathode 14b tapers from a minimum at the periphery 20b of the diaphragm 20, to a maximum at the neck region 20a of the diaphragm 20. Thus, as explained above, oxide formation occurs most rapidly at the periphery

20b of the diaphragm 20 than at the neck region 20a of the diaphragm 20.

It is possible to operate the first and second

5 electrochemical cells at different current densities. Thus,
the oxide layers formed on the outer and inner surfaces of
the diaphragm may be formed with different thicknesses.

Figure 2 illustrates a sectional view of an anodised

10 loudspeaker diaphragm 20. As shown in the drawing, the
 loudspeaker diaphragm 20 has a neck region 20a, and a
 conical region 20c. The loudspeaker diaphragm 20 is provided
 with an oxide layer 20d. The oxide layer 20d is thinner in
 the neck region 20a of the diaphragm 20 than at the

15 periphery 20b of the diaphragm 20. In fact, the oxide layer
 20d may be approximately 2 microns thick at the neck 20a and
 start 20e of the conical region 20c of the diaphragm 20. The
 oxide layer 20d in the conical region 20c, however, may
 taper to a maximum value of approximately 10 microns at the

20 periphery 20b of the diaphragm 20.

The thickness of the aluminium substrate in the conical region 20c of the diaphragm 20 is tapered in reverse, from a minimum value of 0.11 mm at the periphery 20b of the

25 diaphragm 20 to a maximum value of 0.118 mm at the start 20e of the conical region 20c. This reverse taper is formed as a result of the anodising process. When a metal (e.g. aluminium) diaphragm is anodised, some of the metal at the surface of the diaphragm is consumed to form the anodically formed oxide layer. Thus, the metal diaphragm becomes thinner in the regions where the anodically formed oxide

layer is applied. The thicker the oxide layer, the thinner the aluminium substrate becomes.

Reference is now made to Figure 3, which depicts a cell comprising an aluminium cathode 100, a mask 110, and an inlet for an electrolyte 112. The substrate to be anodised is an aluminium disc 114, and this is employed as the anode of the cell.

#### Example 1

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In this example, a 75mm diameter aluminium disc was connected as the anode of the cell depicted in Figure 3. A 75 mm diameter polypropylene disc having a central opening of 10 mm diameter was employed as the mask 110. The distance between the disc and the mask was kept at 3mm. An electrolyte of sulphuric acid (50 degrees C) was pumped into the cell at a rate of 3.0m³ per hour through the central opening of the polypropylene disc. The aluminium disc was anodised at a current density of 90 amps per dm².

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After 20 seconds, an oxide layer was formed on the upper surface of the disc. The thickness of the oxide layer tapered from a maximum of 20 microns at the periphery of the disc to a minimum of 2 microns at the centre of the disc. This variation in thickness was believed to arise because the current path length between the disc and the cathode tapered from a minimum at the periphery of the disc to a maximum at the centre of the disc.

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#### Example 2

The procedure of Example 1 was repeated using a 100 mm diameter aluminium disc as the anode. After 20 seconds, an oxide layer was formed on the upper surface of the disc. The oxide layer was uniform in thickness (10 microns) at the periphery of the disc. This uniform region was 15mm wide. The oxide layer in this region was believed to be uniform in thickness because the current path length between this region of the anode and the cathode was substantially constant. The oxide layer on the remainder of the disc, however, tapered to a minimum value of 2 microns in the central region of the disc. This was believed to be because the current path length in this region tapered to a maximum value at the centre of the disc.

Example 3

The procedure of Example 2 was repeated using a mask formed of a 50 mm diameter polypropylene disc immediately surrounded by a 100 mm diameter aluminium ring. The aluminium portion of the mask was connected to the cathode.

After 20 seconds, an oxide layer was formed on the upper surface of the disc. The oxide layer at the periphery of the disc had a uniform thickness of 10 microns. This uniform

25 region was 50 mm wide. The oxide layer in this region was believed to be uniform in thickness because the current path length between this region of the anode and the cathode was substantially constant. Thus, the aluminium portion of the mask acted as a cathode.

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The oxide layer on the remainder of the disc tapered to a minimum thickness of 2 microns at the centre of the disc.

This was believed to be because the current path length in this region tapered to a maximum value at the centre of the disc.

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#### Example 4

In this example, a 75mm diameter aluminium cone was connected as the anode of the first electrochemical cell described with reference to Figure 1. A 65 mm diameter polypropylene cone was employed as mask 24a. The distance between the cone and the mask was kept at 3mm\*. An electrolyte of sulfuric acid (50 degrees C) was pumped into the cell at a rate of 3.0m³ per hour. The aluminium cone was anodised at an average current density of 90 amps per dm².

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After 20 seconds, an oxide layer was formed on the surfaces of the cone. The thickness of the oxide layer tapered from a maximum of 20 microns at the periphery of the cone to a minimum of 2 microns at the neck (centre) of the cone.

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\*this is the static value; because of the flimsy nature of the cone and the turbulent flow of the acid it is likely that the actual spacing varied somewhat.

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#### Example 5

In this example, a 75mm diameter aluminium cone was
connected as the anode of the first-electrochemical cell
described with reference to Figure 1. The mask 24a was
formed of a 65 mm diameter cone having a polypropylene cone

portion and a peripheral portion formed of aluminium. The peripheral portion was 10mm wide, and was electrically connected to the cathode.

The distance between the mask 24a and the aluminium cone tapered from a maximum value of 3mm\* at the periphery of the mask 24a to a minimum of 1mm\* at the apex 24a pf the mask.

An electrolyte of sulfuric acid (50 degrees C) was pumped into the cell at a rate of 3.0m³ per hour. The aluminium cone was anodised at an average current density of 90 amps per dm².

After 20 seconds, an oxide layer was formed on the surface of the cone. The thickness of the oxide layer was roughly constant at ten microns from the periphery down to a cone diameter of approximately 35 mm, thence tapered to a minimum of 2 microns at the neck (centre) of the cone.

\*these are the static values; because of the flimsy nature

20 of the cone and the turbulent flow of the acid it is likely
that the actual spacing varied somewhat

#### Claims

- 1. A process for forming a coating on a substrate, said process comprising:
- providing an electrochemical cell comprising a cathode and an electrolyte,

connecting a substrate to be oxidized as the anode of the cell,

passing a current through the cell, such that a coating 10 is formed on the substrate, and

controlling the current density distribution within the cell, such that the coating is formed more rapidly in one region of the substrate than in another region of the substrate.

- 15 2. A process as claimed in claim 1, wherein the coating is an oxide layer.
  - 3. A process as claimed in claim 2, wherein the oxide layer is formed by anodising.
  - 4. A process as claimed in any preceding claim, wherein the current density distribution within the cell is controlled by operating the cell at a current density of at least 5 Amps per dm<sup>2</sup>, and by ensuring that the current path length between the cathode and the anode varies from one
  - 5. A process as claimed in claim 4, wherein a mask is positioned between the cathode and the anode to control the

30 current path length between the cathode and the anode.

region of the anode to another.

6. A process as claimed in claim 5, wherein the mask is formed at least in part of a plastic material.

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- A process as claimed in any preceding claim, wherein the current density distribution within the cell is
   controlled, such that the rate of formation of the coating tapers from a maximum value in one region of the substrate to a minimum value in another region of the substrate.
- 8. A process as claimed in any preceding claim, wherein the cell is operated at a current density from 20 to 200 amps per dm<sup>2</sup>.
  - 9. A process as claimed in claim 8, wherein the current density is from 60 to 150 amps per  $dm^2$ .
- 10. A process as claimed in any preceding claim, wherein the electrolyte is at a temperature of from 0 to 100 degrees C.
- 20 11. A process as claimed in claim 10, wherein the electrolyte is at a temperature of from 40 to 80 degrees C.
  - 12. A process as claimed in any preceding claim, wherein a flow of electrolyte is passed over the substrate.
  - 13. A process as claimed in claim 12, wherein the electrolyte is passed over the substrate at a surface velocity of 10 to 1000 metres per minute.
- 30 14. A process as claimed in any preceding claim, wherein the substrate is formed of aluminium, titanium, magnesium or

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an alloy containing at least one of aluminium, titanium and magnesium.

15. A process as claimed in any preceding claim, wherein 5 the substrate is a loudspeaker diaphragm.

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- 16. A process as claimed in claim 15, wherein said coating is formed on both the inner and the outer surface of the diaphragm.
- 17. A process as claimed in claim 16, wherein a first power supply is coupled to the inner surface of the diaphragm and the cathode, and a second power supply is coupled to the outer surface of the diaphragm and a further cathode.
- 18. A process as claimed in claim 17, which comprises operating the first power supply at the same current density as the second power supply.
- 20 19. A process as claimed in claim 17, which comprises operating the first power supply at a different current density as the second power supply.
- 20. A process as claimed in any one of claims 16 to 19,25 wherein the same electrolyte is employed to form the coating on the inner and outer surfaces of the diaphragm.
  - 21. A process as claimed in any one of claims 15 to 20, wherein the coating is formed more rapidly in one region of the loudspeaker diaphragm than in another region of the loudspeaker diaphragm.

22. A process as claimed in claim 21, wherein the rate of coating formation tapers from a maximum value in one region of the diaphragm to a minimum value in another region of the diaphragm.

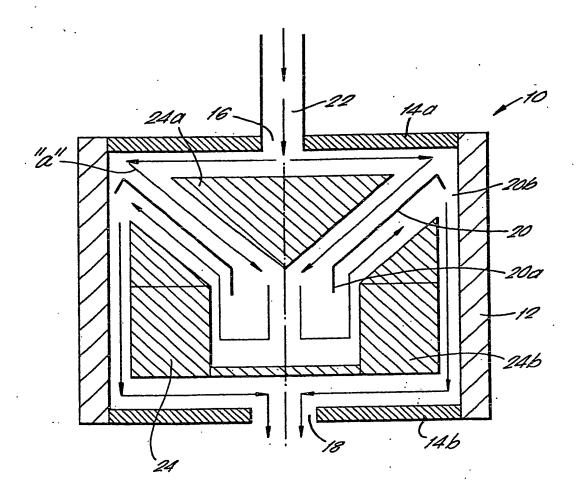
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23. A process as claimed in claim 22, wherein the coating tapers from a maximum value at the periphery of the loudspeaker diaphragm to a minimum value in the neck region of the loudspeaker diaphragm.

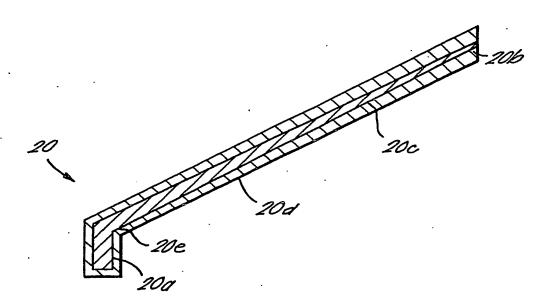
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- 24. A process as herein described, and with reference to the accompanying drawings.
- 25. An anodised substrate whenever produced by a process as claimed in any of claims 1 to 24.
  - 26. An anodised substrate as claimed in claim 25, which is or is part of a loudspeaker diaphragm.
- 20 27. A loudspeaker comprising the loudspeaker diaphragm of claim 26.

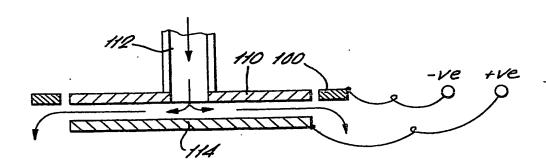
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